

PATENT SPECIFICATION

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(54) MERCAPTO FURANE AND MERCAPTO THIOPHENE DERIVATIVES

(71) We, UNILEVER LIMITED, a company registered under the laws of Great Britain, of Port Sunlight, Birkenhead, Cheshire, England, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

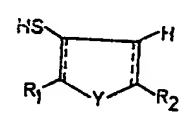
The invention relates to food flavouring substances, their preparation and their use in the flavouring of foodstuffs. In particular the invention is concerned with substances capable of imparting a savoury flavour, for example a flavour resembling that of roast, fried or boiled meat, to foodstuffs. The invention furthermore relates to foodstuffs to which such a flavour has been imparted or in which such a flavour is enhanced by judicial incorporation of these flavouring substances.

Flavouring is understood to be the incorporation of compounds having flavouring characteristics *per se* as well as the incorporation of precursor compounds which do not themselves possess flavouring characteristics but which during the preparation of the foodstuff release or are converted into products having flavouring characteristics.

It has now been found that certain novel mercapto furan and mercapto thiophene derivatives possess flavour characteristics remarkably similar to that of prepared meat or meat products and which are valuable as food flavouring agents. The invention provides

novel sulphur containing heterocyclic compounds of the general formula

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in which Y represents an oxygen or sulphur atom and R¹ and R² a hydrogen atom, a methyl group or an ethyl group, the total number of carbon atoms of R¹ and R² together being at least one and in which no more than one of the dotted lines between carbon atoms 2 and 3, or 4 and 5 represent either an additional carbon to carbon bond between these atoms or that instead these carbon atoms carry each a hydrogen atom.

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As is apparent from the above general formula these compounds may show thioketothicenol tautomerism, e.g. if a carbon to carbon double bond is present adjacent to the mercapto group, and the invention also provides structures of the corresponding thioketo-structure.

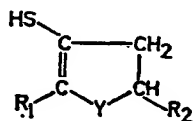
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In an embodiment of the invention substances are provided in which the dotted line between carbon atoms 2 and 3 represents an additional bond between said carbon atoms. Such compounds satisfy the general formula given below in which R¹, R² and Y represent groups indicated above. The embodiment in

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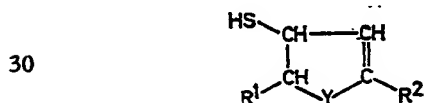
which the total number of carbon atoms of groups R^1 and R^2 taken together is one is preferred.



- 5 Examples of compounds of this class are:
- 3 - mercapto - 2 - methyl - 4,5 - dihydrofuran
 - 3 - mercapto - 5 - methyl - 4,5 - dihydrofuran
 - 3 - mercapto - 2 - methyl - 4,5 - dihydrothiophene
- 10 3 - mercapto - 5 - methyl - 4,5 - dihydrothiophene
- 3 - mercapto - 2,5 - dimethyl - 4,5 - dihydrofuran
 - 3 - mercapto - 2,5 - dimethyl - 4,5 - dihydrothiophene
- 15 3 - mercapto - 5 - ethyl - 4,5 - dihydrofuran
- 3 - mercapto - 2 - ethyl - 5 - methyl - 4,5 - dihydrothiophene

- 20 In another embodiment of the invention substances are provided in which the dotted line between carbon atoms 4 and 5 represents an additional bond between said carbon atoms. Such compounds satisfy the general formula given below, in which R^1 , R^2 and Y represent
- 25 groups indicated above. The embodiment in which the total number of carbon atoms of groups R^1 and R^2 taken together is one is preferred.

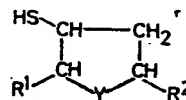
Examples of compounds of this class are:



- 3 - mercapto - 2 - methyl - 2,3 - dihydrothiophene
 - 3 - mercapto - 5 - methyl - 2,3 - dihydrothiophene
- 35 3 - mercapto - 2,5 - dimethyl - 2,3 - dihydrofuran
- 3 - mercapto - 2 - methyl - 2,3 - dihydrofuran
 - 3 - mercapto - 5 - methyl - 2,3 - dihydrofuran
- 40 3 - mercapto - 5 - ethyl - 2,3 - dihydrothiophene
- 3 - mercapto - 2 - ethyl - 5 - methyl - 2,3 - dihydrofuran

- 45 In another embodiment of the invention substances are provided in which there are no additional double bonds between carbon atoms 2 and 3 or 4 and 5. Such compounds satisfy the general formula given below, in which R^1 , R^2 and Y represent groups indicated above.
- 50 The embodiment in which the total number

of carbon atoms of groups R^1 and R^2 taken together is one is preferred.



- Examples of compounds of this class are:
- 3 - mercapto - 2 - methyl - tetrahydrofuran (cis and trans)
 - 3 - mercapto - 5 - methyl - tetrahydrofuran (cis and trans)
 - 3 - mercapto - 2,5 - dimethyl - tetrahydrofuran
 - 3 - mercapto - 5 - methyl - tetrahydrothiophene (cis and trans)
 - 3 - mercapto - 2 - methyl - tetrahydrothiophene (cis and trans)
 - 3 - mercapto - 2,5 - dimethyl - tetrahydrothiophene
 - 3 - mercapto - 5 - ethyl - tetrahydrofuran (cis and trans)
 - 3 - mercapto - 2 - ethyl - 5 - methyl - tetrahydrothiophene
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- 60
- 65
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The above formulae and systematic names have been represented in the form of the most probable tautomeric structure.

The compounds mentioned above show a pronounced roast or fried meat flavour and are consequently valuable flavouring agents for various foodstuffs.

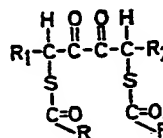
The invention also comprises the flavouring of foodstuffs in which the compounds mentioned above have been incorporated. The flavouring compounds may be added *per se*, or formed in situ, e.g. by incorporating an effective amount of a precursor yielding one or more of the above-mentioned flavouring compounds upon preparation of the foodstuff in a form suitable for consumption.

Suitable precursor compounds are the acetoxy derivatives, in particular 3 - thioacetoxy - 2 - methyl - 4,5 - dihydrofuran and 4 - acetoxy - 5 - methyl - 2,3 - dihydrofuran - 3 - one.

The flavouring characteristics of compounds satisfying the above general formulae and their tautomers were found to be particularly interesting in the case where R^1 and R^2 each represent a hydrogen atom, or a methyl group.

Flavouring compounds mentioned above can be prepared by various methods, as e.g.

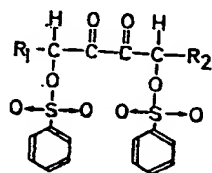
- I. A diketo dithioester of the general formula



in which R represents an alkyl group,

preferably C_2-C_1 , can be cyclized into a thiophenone under the influence of protons in an aqueous medium, and the thiophenone isolated.

- 5 II. A diketo dithioester, e.g. a ditosylate of the formula



can be cyclized with disodium sulphide in an aqueous medium, and the thiophenone isolated.

- 10 III. Cyclic compounds with a sulphur atom attached to a saturated carbon atom are synthesized by reacting the corresponding halogeno compound with potassium thiolacetate in acetone or dimethylformamide and subsequent hydrolysis with sodium methoxide in methanol.

- 15 IV. Cyclic compounds with a sulphur atom attached to a saturated carbon atom with less than two double bonds in the ring structure are synthesized by the following reaction path:

the corresponding ketone is reduced by LiAlH_4 , converted into their p-toluene sulfonic esters and subsequently into the thioacetate. Hydrolysis then yielded the sulphur compound.

- 20 V. Cyclic compounds with a sulphur atom attached to an unsaturated carbon atom are synthesized by the reaction of the corresponding ketone with hydrogen sulphide in ethanol saturated with hydrogen chloride and ether at -80°C .

- VI. Thioketones or compounds with a sulphur atom attached to an unsaturated carbon atom are obtained by reacting the corresponding ketone with phosphorus pentasulphide in toluene at reflux temperature.

A preferred method for preparing mixtures in which several flavouring compounds according to the invention occur is reacting furanone compounds with hydrogen sulphide: suitable furanone compounds are

4 - hydroxy - 5 - methyl - 2,3 - dihydrofuran - 3 - one

4 - hydroxy - 2,5 - dimethyl - 2,3 - dihydrofuran - 3 - one

4 - hydroxy - 2 - methyl - 5 - ethyl - 2,3 - dihydrofuran - 3 - one

4 - hydroxy - 5 - methyl - 2 - ethyl - 2,3 - dihydrofuran - 3 - one

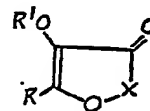
4 - hydroxy - 2,5 - diethyl - 2,3 - dihydrofuran - 3 - one

4 - acetoxy - 5 - methyl - 2,3 - dihydrofuran - 3 - one

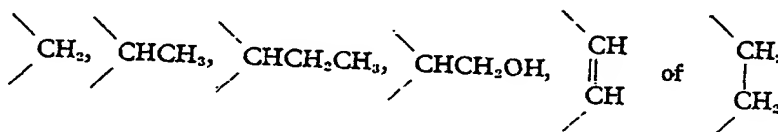
4 - methoxy - 2,5 - dimethyl - 2,3 - dihydrofuran - 3 - one

Of these furanones, the first three named examples are the most preferred.

Our copending application 34141/69 (Serial No. 1283913) claims a process for the preparation of a flavour substance, in which process an heterocyclic ketone having the structure:

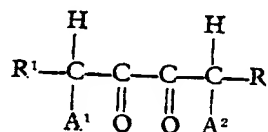


where x is one of the groupings:



- and where R is an alkyl radical having from 1—4 carbon atoms, and where R' is hydrogen, or an acyl radical having from 2—7 carbon atoms or an alkyl radical having from 1—4 carbon atoms, is reacted in the presence of water with hydrogen sulphide or other sulphur-containing compound which is capable of liberating hydrogen sulphide under the reaction conditions.

The alkyl substituted furanones which are used according to the present invention can be prepared by heating and reacting a diketo diester of the general formula:



in which R^1 and R^2 represent a hydrogen atom or an alkyl radical containing 1 or 2 carbon atoms, with the provision that the number of carbon atoms of R^1 and R^2 together is at least one and A^1 and A^2 represent acid radicals. The acid radicals may be derived from carboxylic acids, especially from lower aliphatic

carboxylic acids. Preferred ester groups are those derived from acetic and propionic acid.

The reaction is carried out in an aqueous acidic medium which contains at least 50 percent by volume, preferably at least 75 percent of water, the remainder being a water-miscible polar solvent as, for example a lower aliphatic alcohol such as methanol and ethanol.

The acidic compound available in the aqueous acidic medium may comprise an inorganic acid, a carboxylic acid, or, for example, an organic sulphonic acid. Suitable acids include hydrobromic or hydrochloric acid, sulphuric acid, phosphoric acid, formic acid, acetic acid, propionic acid, p-toluene sulphonic acid and the like. Polycarboxylic acids and hydrocarboxylic acids are less suitable. The use of strong acids, showing a pH value below 5 or rather below 4, is particularly preferred.

The amount of acid in the aqueous medium is not particularly critical and may vary widely. Good results have been obtained with amounts of 0.1—5 equivalents of acid per litre medium. Also the concentration of the diketo diester in the aqueous medium may vary widely. Generally, less than 200g of diketo diester are dissolved per litre of medium. For practical reasons, in particular to reduce the volume of the reaction mixture, the use of too dilute solutions is avoided. A practical range is from 10—100g of diketo diester per litre medium.

The reaction temperature and time of reaction are related. For convenient reaction periods in the range of 0.5—10, preferably from 1—5 hours, it is preferred to conduct the reaction at temperatures above 75°C, preferably at boiling temperature at atmospheric pressure. It is however possible to obtain a satisfactory conversion at lower temperatures, for example of about 50°C, provided the reaction period is suitably adjusted to at least 20 hours.

After termination of the reaction the aqueous reaction mixture is allowed to cool and the desired furanone derivative is isolated in a conventional way. This could be done, for example, by extraction with ether, drying of the ethereal solution and evaporation of the solvent. Undesired polymeric contaminants are removed by distillation of the product under diminished pressure.

Esterification or etherification of the hydroxyl group in the 4-position may be achieved by conventional methods.

The diketo diester starting materials for the process according to the invention can be prepared in various ways. A convenient method is via acetylenic compounds.

60 Step 1—Preparation of an alkyne diol.

Acetylene was coupled with two moles of aldehyde using two moles of a Grignard compound. This method is described in Bull. Soc. Chim.—France 425 (1956). Alternatively a

1-alkyne-3-ol could be coupled with formaldehyde as described in Annalen 596 525 (1955) or by coupling a 1 - alkyne - 3 - ol and other aldehydes or ketones (as described in Bull. Soc. Chim. supra).

Step 2—Esterification of the alkyne diol.

The diacetates were conveniently prepared by reacting with acetic anhydride in the presence of e.g. pyridine or sodium acetate.

Step 3—Oxidation of the alkyne diester

The alkyne diester was oxidized with dilute aqueous potassium permanganate at a low temperature yielding the diketo diester. This method has been described in Bull. Soc. Chim. (France) 789 (1949).

The sulphur containing compound with which the furanone or pyrone is reacted is hydrogen sulphide, in the form of a gas, liquid or solution, or an organic or inorganic compound which is capable of liberating hydrogen sulphide, either in gaseous or nacent form, under the reaction conditions.

Suitable examples of organic sulphur-containing compounds are cysteine, or a peptide containing cysteine such as glutathione, cystine mercaptoacetamide, thioacetamide or salts, for example potassium or sodium salts, hydrochlorides, esters or other simple derivatives of these sulphur-containing compounds.

Suitable examples of inorganic sulphur-containing compounds are sulphides or hydrosulphides of alkali metals, alkaline earth metals or ammonia, such as sodium sulphide, potassium sulphide, ammonium sulphide, calcium sulphide or the corresponding hydrosulphides. Also, other inorganic metallic sulphides, for example ferrous sulphide, may be used.

The reaction mixture comprising at least one ketone and hydrogen sulphide or a sulphur-containing compound as herein defined which react to form the flavour substances according to the invention, may optionally also contain other ingredients which improve or enhance the character of the flavour which subsequently is produced. These optional ingredients may be added before, during or after the ketone and hydrogen sulphide or sulphur-containing compound react.

Thus it is possible to include in the reaction mixture amino acids, the preferred amino acids being one or more of the following: arginine, glutamic acid, proline, glycine, α -alanine, β -alanine, threonine, lysine, leucine, iso-leucine, serine, valine, histidine, cysteine and cystine or a salt thereof. Cysteine and cystine may of course serve in the reaction as sulphur-containing compounds according to the invention.

It is also possible to include in the reaction mixture as an optional ingredient a monosaccharide or a carbohydrate which is capable of being hydrolysed to a monosaccharide under the conditions of the reaction. The most suitable monosaccharides are hexoses, such as

glucose, and pentoses, such as ribose, xylose, rhamnose and arabinose.

It is also possible to conduct the reaction in the presence of C_{12} — C_{18} aliphatic fatty acid, for example, palmitic acid or oleic acid or a salt, ester or glyceride thereof.

The proportions of the ketone to hydrogen sulphide or sulphur-containing compound which are present in the reaction mixture may vary widely. Thus it is possible to use proportions on a weight basis of from 1 part ketone and 50 parts hydrogen sulphide or sulphur-containing compound to 50 parts ketone and 1 part hydrogen sulphide or sulphur-containing compound. Preferred weight proportions are between 1 part ketone and 10 parts hydrogen sulphide or sulphur-containing compound to 10 parts ketone and 1 part hydrogen sulphide or sulphur-containing compound.

Where the reaction conditions are such that excess hydrogen sulphide remains after the reaction is complete, it is advisable to allow the reactants to stand, or to apply ventilation or other means to remove the excess hydrogen sulphide, otherwise the flavour substance may be objectionable due to residual hydrogen sulphide.

The reaction should be conducted under conditions in which at least a trace amount of water is present in the reaction mixture; suitably the amount of water present should be at least equal by weight to the amount of hydrogen sulphide or the sulphur-containing compound. It is however preferred for reasons of convenience that the weight of water should be at least equal to that of the reactants, so that intimate mixing of the ingredients is thereby facilitated. In general it is not necessary that the weight of water present should exceed 100 times that of the reactants, primarily to facilitate subsequent concentration of the flavouring substances which are the products of the reaction. It is also possible to conduct the reaction where the water is bound in the form of water of crystallisation. As an example, sodium sulphide nonahydrate may be employed in the reaction to act both as a sulphur containing compound and as a source of water.

The rate at which the ketone and hydrogen sulphide or sulphur-containing compound react is dependent on the temperature of the reaction mixture, higher temperatures in general resulting in a faster rate of reaction. However, we have found that it is possible to obtain the flavour substances according to the invention by employing a reaction temperature of between 0° and 150°C , but for practical purposes it is preferred and is more convenient to employ a temperature in excess of 60°C , and most preferably between about 90° and 110°C . This is particularly applicable when the reaction is carried out by refluxing at atmospheric pressure.

It is necessary to apply a pressure above that of atmospheric pressure when aqueous

systems are heated at a temperature above the boiling point of the system at atmospheric pressure. It has also been found advantageous to employ superatmospheric pressures when one of the reactants is a gas, for example when gaseous hydrogen sulphide is employed.

When the reaction is conducted in the presence of more than a trace amount of water, the pH of the reaction mixture may vary over a wide range of values. The reaction thus may be conducted at pH values ranging from 2 to 10, but values between 4 and 7 are preferred.

The duration of the reaction may vary considerably and is, of course, dependent on other parameters which control the rate of reaction. We have, for example, found that the flavour substances are produced within a few minutes of commencing the reaction and continue to build up in the reaction mixture for several days. As a general guide, we have found that for a reaction temperature of 100°C , a reasonable reaction time is from 1 minute to 15 hours, whereas at room temperature, the flavour composition may be produced in as little as 3 minutes to as long as 30 days. It is, however, preferred to restrict the reaction time to between 1 and 6 hours.

According to a preferred embodiment of the invention, a ketone and a sulphur-containing compound giving rise to hydrogen sulphide are reacted together in the presence of water by boiling or simmering under reflux at a temperature slightly in excess of 100°C for about 3 hours. The aqueous reaction mixture may subsequently be concentrated to a paste or dried to powder, care being taken to ensure that the loss of volatile components of the flavouring substance so produced is kept to a minimum.

The flavouring substances prepared according to the invention may thus be employed in liquid or semi-liquid form, for example as solutions, emulsions or pastes, or in dried form, for example as a powder. Drying of the reaction products may be accomplished for example by freeze-drying which has been found to be most suitable for optimum retention of flavour volatiles.

The flavouring substances thus prepared may be blended with a further quantity of a ketone as herein defined, which itself is capable of imparting a savoury taste to a foodstuff, or with one or more compounds from the following classes of substances:

I. Amino acids which may be obtained by hydrolysis, autolysis or fermentation or by combination of these from vegetable or animal proteins such as gluten, casein, soyabean protein and the like.

II. Nucleotides, such as adenosine - 5'-monophosphate, guanosine - 5' - monophosphate, inosine - 5' - monophosphate, xanthosine - 5' - monophosphate, uridine - 5' - monophosphate, cytidine - 5' - monophosphate, or

- their amides, deoxy derivatives or their salts. Combinations of nucleotides, for example guanosine - 5' - monophosphate and inosine-5-monophosphate are particularly suitable.
- 5 III. Carboxylic acids such as lactic acid, glycolic acid and γ -hydroxy butyric acid on one hand and dicarboxylic acids such as succinic acid and glutaric acid on the other hand, and especially mixtures of carboxylic acids
- 10 in which succinic acid and lactic acid occur in weight ratios of 1:30 to 1:50.
- IV. Pyrrolidone carboxylic acid or precursors thereof.
- 15 V. Peptides such as alanyl-alanine, alanyl-phenylalanine, alanyl-asparagine, carnosine and anserine.
- VI. Sweetening substances, both artificial, such as saccharine and cyclamate, and natural, particularly mono- and disaccharides.
- 20 VII. Substances with the flavour of cooked or roast meat or of meat broth, (other than those which result from the reaction of a ketone with a sulphur-containing compound as hereinbefore defined), for example the reaction
- 25 products of amino acids such as cysteine or cystine with reducing sugars, or ascorbic acid, or the reaction products of hydrogen sulphide with lower aliphatic aldehydes and ketones, such as propionaldehyde, crotonaldehyde,
- 30 methional, mercapto-acetaldehyde.
- VIII. Volatile sulphur compounds, such as hydrogen sulphides, mercaptans, disulphides and sulphides, such as dimethyl sulphide and diallyl sulphide.
- 35 IX. Guanidines, such as creatine and creatinine.
- X. Salts such as sodium chloride, disodium hydrogen phosphate, monosodium dihydrogen phosphate or other alkali or ammonium phosphates and organic phosphates, such as phosphorus-containing amino acids.
- 40 XI. Nitrogen-containing compounds, such as ammonia, amines, urea, indole and skatole.
- XII. Saturated or unsaturated carboxylic
- 45 acids for example those containing from 2 to 12 carbon atoms in the molecule.
- XIII. Saturated or unsaturated higher hydroxycarboxylic acids and γ and δ -lactones derived therefrom, such as deca- and dodeca-
- 50 5 - olide and 2,3 - dimethyl - 2,4 - alkadiene-4-olides.
- XIV. Lower saturated and unsaturated aldehydes, for example acetaldehyde, propionaldehyde, iso-butyraldehyde and hepten-4-al.
- 55 XV. Lower saturated and unsaturated ketones, such as acetone, butanone and diacetyl.
- XVI. Tricholomic acid and biotenic acid or their salts.
- 60 XVII. Aromatic and/or heterocyclic compounds, such as ortho amino-acetophenone, N-acetonyl pyrrole, iso-maltol, lenthionine, hypoxanthine, guanine, inosine and guanosine.
- XVIII. Lower saturated and unsaturated
- 65 alcohols, such as ethanol and octanol.
- XIX. Colouring substances, such as curcuma and caramel.
- XX. Thickening agents such as gelatin and starch.
- XXI. Unsaturated C_{12} — C_{18} aliphatic fatty
- 70 acids and their glycerides or saturated glycerides.
- The proportions of these optimally added substances used is dependent on the kind of flavour desired and also on the nature of the
- 75 foodstuff to which they are added together with other ingredients, such as herbs and spices.
- In addition to preparing flavouring substances for subsequent addition for foodstuffs, by reacting together a ketone and hydrogen sulphide as herein described, it is also possible to add the unreacted starting materials to the foodstuff so that the flavouring substances may subsequently develop in the foodstuff before
- 80 consumption. Thus, for example, it is possible to add a ketone and a sulphur-containing compound capable of producing hydrogen sulphide to the ingredients of a soup which is subsequently canned and heat sterilised. A desirable
- 85 roast meat-like flavour may thereby be developed within the soup after heat sterilisation in the sealed can.
- The flavouring substances prepared according to the invention may otherwise be incorporated into foodstuffs, such as soups, sausage, reformed comminuted meat, simulated meat
- 90 products, such as textured vegetable protein, and pastry products, in an amount sufficient to impart or enhance the desired flavour. Thus, flavouring amounts will vary according to the individual palate and according to the nature
- 95 of the foodstuffs. As a general guide, the flavouring substances in amounts of from 1 ppm to 8,000 ppm have been incorporated in foodstuffs, these proportions being expressed
- 100 on a weight basis.
- As an illustration of suitable quantities of the flavouring substances that may be added to specified types of foodstuffs, we have found that as little as 1 ppm to 10 ppm w/w is
- 105 sufficient to impart a pleasant roast meat flavour to soups which are bland or otherwise lightly flavoured. On the other hand, when incorporating a similar roast meat flavour to already flavoured food stuffs such as those
- 110 based on vegetable protein, it may be necessary to incorporate larger amounts, for example from 600 to 8,000 ppm w/w of the flavouring substance in order to obtain a desirable flavour.
- In case a pure compound according to claim
- 115 1 is added to a foodstuff, from 0.05 to 50 ppm, preferably from 0.1 to 20 ppm (dry matter content) is added.
- When the flavour substances prepared according to the invention are added to a food-
- 120 stuff, it is believed that further reaction in situ in the foodstuff contributes to the development of the desired flavour characteristic. It would thus appear likely, for example, that sulphhydryl groupings present in or derived from protein
- 125 130

present in the foodstuff react further with the ketone derivatives in the flavour substance to produce compounds having improved flavour properties.

- 5 Examples A1 to A13 describe the synthesis of flavouring compounds according to the invention. Examples B1 to B4 describe the preparation and analysis of mixtures of flavouring compounds according to the invention, and
- 10 Examples C1 to C9 are further examples of the preparation of such mixtures. Examples D1 to D12 illustrate the use of the compounds of the invention in flavouring foodstuffs.

EXAMPLE A1

- 15 Preparation of cis - 3 - mercapto - 2 - methyl-tetrahydrofuran.

2.38 g (19.75 mmol) of trans 3 - chloro - 2 - methyltetrahydrofuran, b.p. 130°C (atm.) n_D^{20} 1.4908, prepared according to the method described by L. Crombie and S. H. Harper, J. Chem.Soc. 1714 (1950) were dissolved in 20 ml of dimethylformamide. 3.42 g (30 mmol) of potassium thiolacetate were added to the solution and the mixture was refluxed for one hour. After cooling, the solvent was distilled off in vacuum and the residue dissolved in 50 ml of water. The aqueous solution was extracted three times with chloroform and the combined extracts were washed with water, dried over anhydrous sodium sulphate and evaporated. The residue was distilled through a 10 cm Vigreux column, yielding 1.71 g of cis - 3 - thioacetoxy - 2 - methyltetrahydrofuran (54%) b.p.=52°—53°C/0.2 mmHg.

- 35 1.5 g (9.2 mmol) of cis - 3 - thioacetoxy - 2 - methyltetrahydrofuran was dissolved in 46 ml of a methanol solution of 0.4 M sodium methoxide and the mixture was allowed to stand overnight at room temperature.

40 Thereafter the reaction mixture was acidified with aqueous sulfuric acid and extracted several times with chloroform. The combined chloroform extracts were washed with water, dried over sodium sulphate and evaporated. The residue was fractionated, using a 10 cm Vigreux column, yielding 0.72 g (67%) of cis - 3 - mercapto - 2 - methyl tetrahydrofuran, b.p. 64—65°C/13 mmHg, n_D^{20} =1.4904.

- 50 Infra-red absorption characteristics of cis - 3 - mercapto - 2 - methyl - tetrahydrofuran: maxima at 2975, 2930, 2870, 2540, 1453, 1385, 1355, 1320, 1110, 1070, 1020, 990 and 850 cm^{-1}

55	i=intensity	m/e	i%	m/e	i%
		84	30	55	40
		74	100	46	30
		73	20	45	80
		59	20	43	90
		56	25	41	100

- 60 Relative retention time as compared with 43.1 minutes found for dodecane was 29.2 minutes.

EXAMPLE A2

Preparation of trans-3-mercapto-2-methyltetrahydrofuran

By the procedure used for the cis-isomer (cf. previous example) 3.92 g (32.5 mmol of cis - 3 - chloro - 2 - methyl tetrahydrofuran b.p. 145°C (atm.) n_D^{20} 1.4520, were treated with potassium thiolacetate affording 2.34 g (45%) of trans - 3 - thio - acetoxy - 2 - methyl-tetrahydrofuran b.p. 49—50°C/3 mmHg. This product (1.8 g) was hydrolysed with sodium methoxide as described in the previous example, yielding 0.85 g of trans - 3 - mercapto-2 - methyltetra hydrofuran b.p. 62°C/20 mmHg, n_D^{20} =1.4798.

Infra-red absorption characteristics: maxima at 2975, 2930, 2870, 2540, 1453, 1385, 1355, 1195, 1140, 1120, 1075, 1018 and 860 cm^{-1} .

mass data:

m/e	intensity %	m/e	intensity %
84	30	55	40
74	100	46	30
73	20	45	80
59	20	43	90
56	25	41	100

Relative retention time as compared with 43.1 minutes found for dodecane was 25.5 minutes.

EXAMPLE A3

Preparation of cis and trans-3-mercapto-5-methyl-tetrahydrofuran.

5 g (50 mmol) of 3 - hydroxy - 5 - methyl-tetrahydrofuran, b.p. 92°C/23mmHg, prepared according to the method of F.C. Hartman and R. Baker, J. Org. Chem. 29, 873 (1964), were dissolved in 30 ml of pyridine and 11.5 g (60 mmol) of p-toluene-sulfonyl-chloride were added at -10°C. The mixture was allowed to stand for 18 hours at room temperature, the reaction mixture was worked up in the usual way, yielding 11.6 g (90%) 3 - p - tolyl-sulfonyloxy-5-methyl-tetrahydrofuran. 10g of the p-toluene sulfonate were dissolved in 80 ml of acetone and treated with 5.7 g (50 mmol) of potassium thiolacetate. After the reaction mixture had remained at reflux temperature for 24 hours, the acetone was removed by evaporation. The residue was dissolved in water and the aqueous solution extracted three times with dichloromethane; the combined extracts were washed, dried and evaporated to dryness. Distillation of the residue gave 5.55 g (89%) of the 3 - thioacetoxy - 5 - methyl-tetrahydrofuran, b.p. 62—63°C/1.3 mmHg.

4.0 g (23 mmol) of the thiolacetate was hydrolysed as described in Example A 6, yielding 2.38 g (80%) of the cis/trans 3-mercapto-5 - methyl - tetrahydrofuran b.p. 57—58°C/14 mmHg; n_D^{20} =1.4795.

Infra-red absorption characteristics: maxima at 2970, 2925, 2860, 2540, 1440, 1380, 1350, 1080, 1050, 1015, 890 and 810 cm^{-1} .

mass data:

	m/e	Intensity (%)	m/e	Intensity (%)
	85	46	54	21
	73	33	47	20
5	60	20	45	48
	59	17	43	72
	55	100	41	100

Relative retention times as compared with 43.1 minutes found for dodecane were 27.3 minutes for the trans compound and 27.7 minutes for the cis compound.

EXAMPLE A4

Preparation of 3-mercapto-2-methyl-4,5-dihydrofuran

- 15 13.65 g (0.1 m) of 3 - chloro - 3 - acetylpropanol (b.p. 90—110°C/2mmHG; n_D^{20} 1.4740) prepared according to the method described by J.R. Stevens and G.A. Stein, J.Am.Chem.Soc. 62, 1045 (1940), were refluxed with 18.6 g (0.15 m) potassium thiolacetate in 100 ml of acetone for about 2 hours. After cooling the reaction mixture was filtered and the filtrate evaporated to dryness and the residue dissolved in water. The aqueous solution was extracted five times with chloroform and the combined extracts washed, dried and evaporated. Distillation of the residue yielded 3 - thioacetox - 2 - methyl - 4,5 - dihydrofuran, b.p. 57—59°C/0.6 mmHg.

- 30 5g (31.6 mol) of 3 - thioacetox - 2 - methyl-4,5 - dihydrofuran were dissolved in 156 ml of a 0.4 N sodium methoxide in methanol and left at room temperature for 24 hours. The reaction product was purified in the usual way affording the title compound which could be isolated by preparative gas chromatography.

- 35 Infra-red absorption characteristics: maxima at 2960, 2920, 2890, 2860, 1740, 1663, 1635, 1480, 1435, 1400, 1380, 1365, 1220, 1060, 1030, 980, 960, 905, 680 cm^{-1} .

mass data:

	m/e	Intensity (%)	m/e	Intensity (%)
	116	70	60	24
	84	22	45	55
45	83	20	43	100
	73	36	42	20
	71	19	41	20

- 50 Relative retention time as compared with 43.1 minutes found for dodecane was 30.6 minutes.

EXAMPLE A5

Preparation of 3-mercapto-5-methyl-4,5-dihydrothiophene.

- 55 2 g of 5 - methyl - tetrahydrothiophene - 3-one (b.p. 68—69.5°C/11 mmHg; n_D^{20} 1.5062) prepared according to the method described by M.A. Gianturco, c.s., Tetrahedron, 20 1763 (1964) were dissolved in 25 ml of ethanol (saturated with hydrogen chloride) and treated with hydrogen sulphide at -80°C according

to the method given by S. Bleisch and Mayer, Chem.Ber. 100, 100 (1967). After purification of the reaction mixture the title compound could be isolated by preparative gas chromatography.

Infra-red absorption characteristics: maxima at 2960, 2920, 2860, 2510, 1540, 1445, 1425, 1400, 1375, 1260, 1205, 1080, 930, 825, 790, 720, 680 cm^{-1} .

mass data:

m/e	Intensity (%)	m/e	Intensity (%)
132	100	84	36
117	95	59	38
99	58	58	28
97	38	45	100
85	37	41	42

Relative retention time as compared with 43.1 minutes found for dodecane was 43.1 minutes.

EXAMPLE A6

Preparation of 3-mercapto-5-methyl-4,5-dihydrofuran

2.75 g 5 - methyl - tetrahydrofuran - 3-one, b.p. 88—89°C/112 mmHg, prepared according to the method described by H. Wijnberg, J. Amer. Chem.Soc. 80, 364 (1958), were dissolved in 3.5 ml of ethanol saturated with HCl gas). The solution was cooled to -80°C and treated with hydrogen sulphide as described by R. Mayer, Angew. Chem., Intern. Edition 3, 277 (1964).

After purification of the reaction product, the title compound was isolated by distillation at reduced pressure under nitrogen and by preparative gas chromatography.

Infra-red absorption characteristics: maxima at 2980, 2930, 2862, 2540, 1620, 1455, 1385, 1270, 1235, 1110, 1080, 1050, 1035, 945, 899, 825, 650 cm^{-1} .

mass data:

m/e	i.%	m/e	i.%	m/e	i.%
116	17	55	11	42	50
73	13	45	32	41	26
72	22	43	100	39	25
71	34				

Relative retention time as compared with 43.1 minutes found for dodecane was 29.0 minutes.

EXAMPLE A7

Preparation of 3-mercapto-2,5-dimethyl-4,5-dihydrofuran.

2.0 g 2.5 - dimethyl - tetrahydrofuran - 3-one (b.p. 143°C/atm.; n_D^{20} 1.4240) prepared according to the method described by G. Dupont, Ann. de Chimie et de Physique, 8^e série, Tome 30, 535 (1913) were converted into the title compound with hydrogen sulphide as described in Example A6. From the reaction product the title compound was isolated by preparative gas chromatography.

Infra-red absorption characteristics: maxima

at 2975, 2925, 2862, 2540, 1610, 1460, 1450, 1378, 1330, 1262, 1218, 938, 875, 830 cm^{-1} .

mass data:

	m/e	i. %	m/e	i. %	m/e	i. %
5	130	14	55	10	43	100
	88	10	53	14	41	13
	87	12	45	20	39	14
	71	24				

Relative retention time as compared with 43.1 minutes found for dodecane was 28.5 minutes.

EXAMPLE A8

Preparation of 3-mercapto-2,5-dimethyl-4,5-dihydrothiophene.

- 15 2,5 - dimethyl tetrahydrothiophene - 3 - one (b.p. 72—82°C/12 mmHg; n_D^{20} 1.4908) were prepared according to the method described by H.A. Gianturco, Tetrahedron 64, 1763 (1964) from 4.6 (0.2 mol) sodium, 26 g (0.2 m) methyl - α - mercapto - propionate and 22 g (0.22 mol) methyl crotonate. After purification the reaction product yielded 39 of an oily residue which, upon distillation, gave 21.7 g (58%) 2,5 - dimethyl - 3 - carbo-methoxy - tetrahydrothiophene - 4 - one, b.p. 80—84°C/O.5mmHg. The decarboxylative hydrolysis of the β -ketoester was effected by refluxing for 1 hour in 10% aqueous H_2SO_4 . After purification the reaction product yielded 2.5 - dimethyl - tetrahydrothiophene-3 - one in nearly quantitative yield; b.p. 80°C/12 mmHg.

The ketone prepared as mentioned above was converted into the title compound and could be isolated by preparative gas chromatography.

Infra-red absorption characteristics: maxima at 2960, 2920, 2882, 2837, 1450, 1440, 1290, 1250, 1210, 1152, 1015, 1000, 688 cm^{-1} .

40 mass data:

	m/e	i. %	m/e	i. %
	146	90	61	25
	131	44	59	100
	113	60	45	55
45	98	38	41	28
	85	24	39	36

i = intensity

Relative retention time as compared with 43.1 minutes found for dodecane was 43.1 minutes.

EXAMPLE A9

Preparation of cis/trans 3-mercapto-2-methyl tetrahydrothiophene.

- 55 23.2 g (0.2 m) of 2 - methyl - tetrahydrothiophene-3-one (b.p. 68—70°C/11 mmHg; n_D^{20} 1.5079) prepared according to the method described by P. Karrer and H. Schmid, Helv. Chim. Acta 27, 124 (1944), dissolved in 150 ml of dry ether were added dropwise in the course of 45 min. to a suspension of 7.8 g

(0.2 m) of LiAlH_4 in 300 ml of dry ether.

After the addition was completed the reaction mixture was refluxed for 2 hours under nitrogen cooled in an ice-bath and a mixture of 30 ml of ethylacetate and 100 ml of ether were added. After filtration, the organic layer was washed with water, dried and evaporated. From the residue the cis/trans mixture of 3-hydroxy - 2 - methyl - tetrahydrothiophene could be isolated.

The cis/trans mixture of the alcohols prepared as mentioned above was converted into their p-toluene sulphonates by the method described earlier.

The p-toluene sulfonic esters were treated with potassium thiolacetate in acetone as described for the preparation of Example A3 and purified in the usual way. After hydrolysis of the thiolacetate with sodium methoxide in methanol for 18 hours at room temperature, water was added and the liquid was extracted with CH_2Cl_2 . After acidification the aqueous phase was again extracted with CH_2Cl_2 . The organic layer was dried with Na_2SO_4 and evaporated, yielding cis/trans 3 - mercapto-2 - methyl - tetrahydrothiophene. The isomers were isolated by gas chromatography as described above.

Infra-red absorption characteristics: cis: maxima at 2962, 2920, 2895, 2865, 1456, 1442, 1376, 1315, 1260, 1200, 1170, 1020, 960, 680. trans: 2962, 2925, 2880, 2850, 1450, 1440, 1379, 1330, 1270, 1200, 670 cm^{-1} .

mass data:

cis-compound		trans-compound	
m/e	i. %	m/e	i. %
134	32	134	82
85	19	74	70
74	38	69	54
69	20	67	35
59	27	59	26
55	28	55	48
47	28	47	26
45	52	45	36
41	100	41	100
39	47	39	45

i = intensity

Relative retention time as compared with 43.1 minutes found for dodecane was for cis 41.6 and for trans 43.8.

EXAMPLE A10

Synthesis of cis/trans 3-mercapto-5-methyl-tetra hydrothiophene.

23.2 g (0.2 m) of 5 - methyl - tetrahydrothiophene-3-one b.p. 88—89°C/112 mmHg were converted with LiAlH_4 into the cis/trans mixture of 3 - hydroxy - 5 - methyl - tetrahydrothiophene by the method described above.

From this alcohol/mixture the p-toluene sulfonic esters were made in the usual way

and the latter were converted into the thioacetates and subsequently into the title compound by hydrolysis with sodium methoxide in methanol. The isolation of 3 - mercapto - 5 - methyl tetrahydrothiophene was achieved by distillation and preparative gas chromatography; n_D^{20} 1.5568.

Infra-red absorption characteristics: maxima at 2958, 2920, 2860, 2540, 1450, 1435, 1375, 1268, 1205, 1182, 1030, 1000, 940, 735, 715, 700 cm^{-1} .

mass data:

	m/e	i.%	m/e	i.%
	134	100	49	88
15	86	42	45	45
	85	46	43	46
	84	62	41	52
	61	36		
	59	38		

20 i=intensity

Relative retention time as compared with 43.1 minutes found for dodecane was 40.5 minutes.

EXAMPLE A11

25 Synthesis of 3-mercapto-2,5-dimethyltetrahydrofuran.

2,5 - dimethyltetrahydrofuran - 3 - one, b.p. 143°C/atm., n_D^{20} 1.4240, were reduced with LiAlH_4 as described above, yielding a mixture of stereoisomers of 3 - hydroxy - 2,5 - dimethyltetrahydrofuran. The latter were converted into the p-toluene sulfonic esters and then subsequently treated with potassium thioacetate. After hydrolysis of the thioacetic ester with sodium methanolate the title compound was isolated by preparative gas chromatography.

Infra-red absorption characteristics: maxima at 2975, 2930, 2870, 2540, 1458, 1448, 1380, 1165, 1125, 1100, 1083, 951, 916, 880 cm^{-1} .

mass data:

	m/e	i.%	m/e	i.%	m/e	i.%
	99	26	73	26	43	53
	98	19	60	24	39	14
45	88	50	55	100		
	83	8	45	18		

i=intensity

Relative retention time as compared with 43.1 minutes found for dodecane was 20.0 minutes.

EXAMPLE A12

Synthesis of 3-mercapto-2,5-dimethyltetrahydrothiophene.

2,5 - dimethyltetrahydrothiophene - 3 - one, b.p. 143°C/atm., n_D^{20} 1.4240, was reduced with LiAlH_4 , converted into the p-toluene sulfonic esters and the thioacetates, and finally into the title compound by the procedure as described above for the corresponding oxygen

compound. The title compound was isolated by preparative gas chromatography.

Infra-red absorption characteristics: maxima at cis: 2965, 2925, 2865, 1458, 1450, 1380, 1310, 1250, 1168, 1025, 1000, 992, 938, 680 trans: 2965, 2920, 2860, 1455, 1448, 1378, 1270, 1190, 1168, 1020, 997, 985 cm^{-1} .

mass data:

m/e	intensity (%)	m/e	intensity (%)	
cis compound		trans compound		
148	36	148	48	70
99	33	99	29	
67	40	67	46	
61	90	61	88	
60	39	60	39	
59	70	59	67	75
55	100	55	100	
45	68	45	53	
41	80	41	70	
39	72	39	58	

Relative retention time as compared with 43.1 minutes found for dodecane was for cis 42.4 and for trans 44.7 minutes.

EXAMPLE A13

Synthesis of 3-mercapto-2-methyl-4,5-dihydrothiophene.

2 g of 2 - methyltetrahydrothiophene - 3 - one b.p. 68—70°C/11 mmHg; n_D^{20} 1.5079, prepared according to the method described by P. Karrer and H. Schmid, *Helv. Chim. Acta*, 27, 124 (1944), was dissolved in 25 ml of ethanol (saturated with hydrogen chloride) and treated with hydrogen sulphide at -80°C as described by R. Mayer, *Angew. Chem., Intern. Edition*, 3, 277 (1964). From the reaction product 3 - mercapto - 2 - methyl-4,5 - dihydrothiophene could be isolated by preparative gas chromatography.

Infra-red absorption characteristics: maxima at 2960, 2930, 2910, 2840, 1585, 1435, 1400, 1375, 1300, 1265, 1149, 1020, 850, 750, 685, 675 cm^{-1} .

mass data:

m/e	i.%	m/e	i.%	m/e	i.%	
132	100	98	28	65	19	
131	29	97	34	59	70	105
99	90	71	23	58	18	
				45	41	

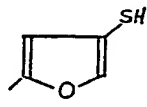
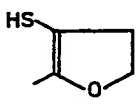
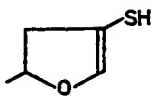
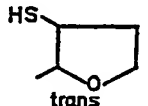
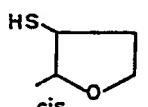
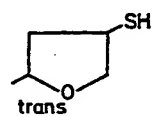
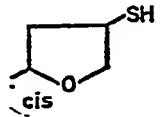
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Relative retention time as compared with 43.1 minutes found for dodecane was 48.0 minutes.

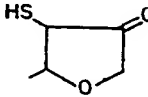
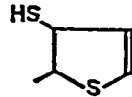
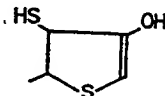
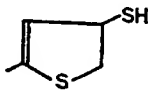
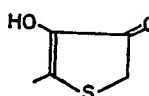
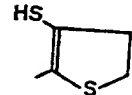
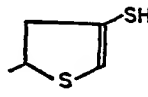
EXAMPLE B1

4 - hydroxy - 5 - methyl - 2,3 - dihydrofuran - 3 - one (0.5 g) was dissolved in water (30 ml) and reacted with hydrogen sulphide (15 g) for 4 hours at 95—100°C in a glass-lined autoclave. At the end of the reaction period the mixture was cooled and poured into

- ice-water (100 ml) and extracted five times with dichloromethane. The combined extracts (125 ml) were concentrated at atmospheric pressure to 10 ml and the concentrated dichloromethane extract was analysed by gas-liquid chromatography on a 600—0,4 cm glass column with Diatoport S as support. The stationary phase was Apiezon L 10% and Carbowax 20 m 1%, the temperature was programmed from 60°—220°C at 4°C/min, the carrier gas was nitrogen with a velocity of 40 ml/min and the recorder speed was 48 cm/h. "Apiezon" and "Carbowax" are Registered Trade Marks. From the exhaust of the gas chromatograph the various microgram samples could be trapped and their infra-red spectra could be obtained from these samples according to the method described by H. Copier and J.H.v.d.Maas, *Spectro Chimica Acta*, 23A 2699 (1967). 20
- The infra-red spectra were determined using a Perkin-Elmer 225 and 257 spectrometer. The mass data were determined using an A.E.I. M.S.—9 instrument at a source temperature of 200°C. with the following procedure: On one of the inlets of the mass spectrometer a capillary with 0.1 ml/minute conductance was mounted. The glass tubes with the absorbed eluent were connected to this capillary by a ground glass joint, a heater was placed around the sample tube and with a stream of helium the compound was flushed into the ion source of the mass spectrometer. 25
- From the reaction mixture the following products could be isolated and identified: 30 35

Mass data m/e and intensity %	Infra-red data (cm ⁻¹)	Ret. time min. *)	Assumed Structure
114 (100), 113 (50) 85 (60), 71 (45), 69 (36), 59 (35), 53 (44), 51 (41), 45 (56), 43 (85)	2950, 2920, 2850, 1585, 1560, 1518, 1510, 1440, 1387, 1225, 1195, 1123, 1088, 1018, 940, 888, 730	26.6	
116 (70), 84 (22), 83, (20), 73(36), 71 (19), 60 (24), 45 (55), 43 (100), 42 (20), 41 (20).	2960, 2920, 2890, 2860 1740, 1663, 1635, 1480, 1435, 1400, 1380, 1365, 1220, 1060, 1030, 980, 960, 905, 680.	30.6	
Corresponding to data of Example A6			
Corresponding to data of Example A2		25,5	
Corresponding to data of Example A1		29.2	
Corresponding to data of Example A3		27.3	
Corresponding to data of Example A3		27.7	

*) As compared with 43.1 min. for dodecane.

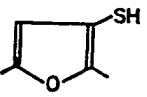
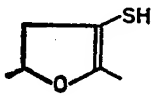
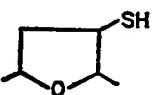
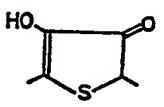
Mass data m/e and intensity %	Infra-red data (cm ⁻¹)	Ret. time min.★)	Assumed Structure
132 (20), 117 (100), 100 (12), 99 (12), 85 (25), 59 (40), 58 (14), 45 (30), 43, (12), 41 (27)		37.5	
133 (62), 130 (60), 129 (55), 117 (47), 97 (65), 85 (55), 60 (67), 59 (94), 43 (35), 41 (52).		40.7	
132 (48), 131 (41), 103 (31), 97 (58), 71 (45), 67 (35), 59 (35), 45 (85), 43 (100), 41 (53),		42.5	
132 (48), 131 (41), 103 (31), 97 (58), 71 (45), 67 (35), 59 (35), 45 (85), 43 (100), 41 (53).	2960, 2910, 2850, 1725 1645, 1420, 1378, 1255, 1115, 940, 780	48.1	
132 (5), 131 (6), 130 (100), 71 (6), 60 (5), 59 (42), 58 (5), 57 (6), 46 (5), 45 (7), 43 (8), 41 (6).	3200, 3000, 2930, 1665, 1615, 1600, 1400, 1368, 1360, 1305, 1190, 1133, 858, 848, 780, 640, 560.	47.0	
Corresponding to data of Example A13		48	
Corresponding to data of Example A5		43.1	

★) As compared with 43.1 min for dodecane.

EXAMPLE B2

4 - hydroxy - 2,5 - dimethyl - 2,3 - dihydrofuran - 3 - one (0.5 g) was treated with hydrogen sulphide (15g) and analysed as

described in example B1. From the reaction product the following components were isolated and identified:

Mass data	Infra-red data	Ret. time min*)	Structure
129 (4.5), 128 (65), 127 (22), 113 (8), 96 (4.5), 95 (10), 85 (25), 45 (10), 43 (100), 39 (9).	3115, 2950, 2920, 2880, 2850, 1567, 1430, 1380, 1365, 1330, 1225, 1115, 1065, 1000, 980, 920, 795, 646, 615.	42	
Corresponding to data of Example A7		28.5	
Corresponding to data of Example A11		29.0	
145 (10, 144 (60), 85 (32), 61 (12), 60 (25), 59 (100), 58 (15), 57 (19), 55 (15), 45 (15).	3300, 2980, 2940, 1670, 1600, 1450, 1430, 1395, 1360, 1265, 1130, 1052, 955, 840, 760.	44.4	

*) As compared with 43.1 min. for dodecane

EXAMPLES B3 AND B4

10 Preparation of Starting Materials

Preparation of 4-hydroxy-5-methyl-2,3-dihydrothiophene-3-one.

140 g of commercially available 1-butyne-3-ol (boiling point 107° at atmospheric pressure) were treated in an aqueous solution with 200 g of a 30% formaldehyde solution in the presence of 10 g CuCl and refluxed for 50 hours. The resulting 156 g (70%) of 2-pentyn-1,4-diol (boiling point 115°C at 2.5 mm mercury) were isolated by evaporating off the water and distilling the residue.

50 g (0.5 m) of 2-pentyn-1,4-diol were dissolved in 250 ml of dry pyridine. The solu-

tion was stirred and cooled to -10° in an ice-salt mixture. With stirring, a cold solution of 286 g (1.5 m) of p-toluene sulfonyl chloride in 550 ml of dry dichloromethane was added dropwise, under exclusion of atmospheric moisture, from the dropping funnel, in such a manner that the temperature did not exceed -5°C. After completion of the addition (about 1.5 hours) stirring at 0° was continued for 5 hours, and water (30 ml) was added in portions at intervals of 5 min., with stirring and cooling, so that the temperature did not rise above 5°. The solution was then poured into 1000 ml of cold water. The mixture was extracted three times with dichloromethane; the combined extracts were successively

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30

35

washed with portions of ice-cold dilute sulfuric acid, water, sodium hydrogen carbonate solution and water. The dichloromethane solution was then dried with anhydrous sodium sulphate and evaporated to dryness, affording a syrup which crystallizes on standing. It was recrystallized from ethanol; yield 125 g = 61%; m.p. 80–85°C.

A solution of the ditosyl compound (98 g = 0.24 m) and potassium thioacetate (60 g = 0.527 m) in dimethylformamide (1.5 l) was stirred for 45 minutes at 40°C under nitrogen, then concentrated under reduced pressure and diluted with water (1 litre). The mixture was extracted five times with dichloromethane, the combined extracts were washed with water, dried with anhydrous sodium sulphate and evaporated to dryness. The residue was distilled through a short path column, affording 43.8 g = 84.5% of the dithioacetate; bp. 129°–130° at 1.6 mm mercury; n_D^{20} = 1.5440. 20 g of the 1,4 - dithioacetoxo - 2-pentynyl were then dissolved in 1000 ml of an alcohol-water mixture (90:10 by volume) and the solution was cooled to -25°C. A solution of 32 g potassium permanganate and 48 g magnesium sulphate heptahydrate in 700 ml of water was slowly added in 2 hours whilst maintaining the temperature at -20 to -25°C.

The reaction mixture was stirred for another 2 hours at the same temperature, and 600 g of ice were then added. The reaction mixture was then extracted with cold chloroform. The light yellow coloured organic solution yielded after drying and evaporation of the solvent 13.5 g = 59% of a yellow oil (pentane - 2,3-dione - 1,4 - dithioacetate).

10 g of the yellow oil thus obtained (pentane - 2,3 - dione - 1,4 - dithioacetate) were dissolved in 1500 ml of 0.5 N aqueous hydrochloric acid and stirred for 1.5 hours at 95°C. After cooling the reaction mixture was extracted five times with chloroform, the combined extracts were washed with water, dried with anhydrous sodium sulphate and evaporated to dryness, affording a sirup which crystallized on standing. After recrystallization, from dichloromethane, white crystals of 4-hydroxy - 5 - methyl - 2,3 - dihydrothiophene-3 - one were obtained; m.p. 152–153°C; yield = 40%.

Infra-red absorption characteristics; maxima at 3200, 3000, 2930, 1665, 1615, 1600, 1400, 1368, 1360, 1305, 1190, 1133, 858, 848, 780, 640, 560 cm^{-1} .

Nuclear magnetic resonance (NMR) data were:

		δ		M	
i=intensity	mass data:	a :	2,24	multiplet	3H
		b :	3,60	"	2H
		m/e	i%	m/e	i%
		132	5	58	5
		131	6	57	6
		130	100	46	5
		71	6	45	7
		60	5	43	8
		59	42	41	6

Preparation of 4-hydroxy-2,5-dimethyl-2,3-dihydrothiophene-3-one
34.2 g of 3 - hexyne 2,5 - diol (boiling point 103° at 2 mm mercury) were dissolved in 200 ml of dry pyridine. The solution was stirred and cooled to -10°C in an ice-salt bath. With stirring a cold solution of 172 g (0.9 mol) of p-toluene sulfonyl chloride in 350 ml of dry dichloromethane was added dropwise (temp. < -5°C). After completion of the addition (2 hours), stirring at 0° was continued for 1 hour, and the solution was

kept overnight at 0°, with the exclusion of moisture. After addition of water (20 ml) in portions, as described above, and stirring for 30 min., the product was isolated, as described above. Recrystallization from dichloromethane/pentane afforded the pure ditosylate with mp. 118–120°C; yield = 101 g (80%).

70 g (0.16 m) of 3 - hexyne - 2,5 - ditosylate were dissolved in a mixture of 1700 ml of ethanol and 750 ml of dioxan. To this solution, which was cooled in ice-water, a solution of 63 g potassium permanganate and

91 g of magnesium sulphate hepta hydrate in 1600 ml of water was added at 20—22°C in the course of 45 min. Stirring was continued for 30 min. and 600 ml of water were added and the brown reaction mixture was extracted five times with 200 ml portions of cold chloroform. The combined extracts were washed with water over anhydrous sodium sulphate and evaporated. The solid residue was recrystallized from tetrachloromethane affording 46 g = 64% of yellow crystals with mp. 128—130° (dec.)

23 g of hexane - 3,4 - dione - 2,5 - ditosylate were dissolved in a mixture of 30 ml water and 50 ml ethanol at 90°C. To this solution

was added 18 g of sodium sulphite nonahydrate. The mixture was stirred at 90° for 1.5 hours and then diluted with 300 ml water. After acidification with diluted hydrochloric acid, the mixture was extracted five times with dichloromethane. The combined extracts were washed with water, dried over sodium sulphate and evaporated. The crystalline residue was recrystallized from dichloromethane-light petroleum; yield = 4.32 g = 60%, m.p. = 77—79°C.

Infra-red absorption characteristics; maxima at 3300, 2980, 2940, 1670, 1600, 1450, 1430, 1395, 1360, 1265, 1130, 1052, 955, 840, 760 cm⁻¹.

NMR data:

 δ

M

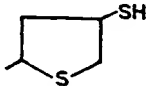
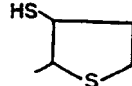
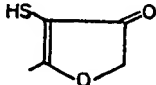
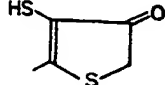
		a :	1,55	doublet	3H				
		b :	2,26	multiplet	3H				
		c :	3,70	"	1H				
		d :	5,6	broad singlet	1H				
<i>i</i> =intensity	mass data:	m/e	<i>i</i> .%	m/e	<i>i</i> .%	m/e	<i>i</i> .%	m/e	<i>i</i> .%
		145	10	61	12	58	15	45	15
		144	60	60	25	57	19		
		85	32	59	100	55	15		

EXAMPLE B5

4 - hydroxy - 5 - methyl - 2,3 - dihydrothiophene - 3 - one (0.5 g) was treated with

hydrogen sulphide (15 g) as described in example B1. From the reaction product the following reaction components were isolated.

35

Mass data	Infra-red data	Ret. time (min*)	Structure
Corresponding to data of Example A10		40.5	
Corresponding to data of Example A9		cis 41.6 trans 43.8	
132 (10), 131 (14), 130 (100), 129 (46), 98 (10), 97 (51), 96 (10), 85 (14), 59 (12), 52 (39), 51 (36), 50 (27), 45(28).	2920, 2850, 2530, 1510, 1435, 1375, 1175, 1090, 890, 855, 715.	34**	
148 (11), 147 (10), 146 (100), 145 (20), 132 (15), 130 (40), 129 (15), 114 (28), 113 (35), 100 (16), 99 (18), 98 (13), 97 (43), 85 (40), 71 (25), 69 (10), 61 (12), 60 (25), 59 (95), 58 (30), 57 (10), 55 (20), 53 (15), 47 (10), 46 (12), 45 (63).	2920, 2860, 2530, 1665, 1565, 1450, 1395, 1375, 1265, 1200, 1150, 1085, 860, 800, 730.	53.4**	

*) As compared with 43.1 minutes for decane.

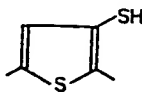
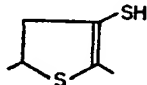
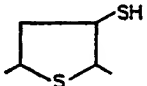
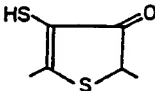
**) As compared with 27.2 minutes for decane.

EXAMPLE B6

4 - hydroxy - 2,5 - dimethyl - 2,3 - dihydrothiophene - 3 - one (0.5 g) was treated with

hydrogen sulphide (15 g) as described in example B 1. From the reaction product the following components were isolated.

5

Mass data	Infra-red data	Ret. time min.*)	Structure
144 (60), 143 (36), 114 (27), 113 (21), 111 (52), 99 (59), 59 (100), 55 (19) 45 (55), 41 (23).	2958, 2920, 2860, 1445, 1378, 1315, 1190, 1153, 1132, 822, 680, 625,	44.5	
Corresponding to data of Example A8		43.1	
Corresponding to data of Example A12		cis 42.4 trans 44.7	
162 (12), 160 (100), 159 (10), 27 (26), 117 (17), 111 (25), 99 (26), 85 (18), 72 (30), 71 (30), 67 (26), 61 (31), 60 (34), 59 (95), 58 (25), 57 (28).	2980,2920, 2860, 2530, 1670, 1565, 1460, 1390, 1375, 1275, 1255, 1130, 1000, 930, 875, 770, 740, 540		

*) As compared with 43.1 min. for dodecane.

EXAMPLE C1

A beef-flavoured composition was prepared by adding 250 ml of water to a mixture of 5.7 g of 4 - hydroxy - 5 - methyl - 2,3 - dihydrofuran - 3 - one and 25.0 g of cysteine and heating the mixture at about 100°C for 2 1/2 hours. The resulting mixture was cooled and quantities of between 0.2 and 2.0 ml of the reaction mixture were sprayed over 100 g portions of dehydrated textured vegetable protein containing no meat. An excellent roast meat flavour was thereby imparted to this material as assessed by eleven out of a total panel of twelve expert tasters.

Dextrin-maltose was added to a portion of the flavoured mixture which resulted from the reaction described above in an amount which provided a composition containing about 70 parts by weight of dextrinmaltose to each part of the substance calculated on a solid basis. The composition was freeze-dried and a beef-flavoured product was obtained.

25

EXAMPLE C2

To 6.4 g of 4 - hydroxy - 2,5 - dimethyl-2,3 - dihydrofuran - 3 - one in a buffer solution containing about 35 g of sodium acetate, about 14 g of acetic acid and 400 ml of water

30

(pH 5.0), a solution of 12 g of sodium sulphide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) in 200 ml of water was added over a period of 30 minutes. The mixture was then boiled under reflux conditions at atmospheric pressure for 2 hours and allowed to cool. The pH was then 6.6. The reaction mixture so obtained had a good roasted meat flavour.

EXAMPLE C3

3.0 of a 70/30 mixture of 4 - hydroxy - 2-methyl - 5 - ethyl - 2,3 - dihydrofuran - 3-one and 4 - hydroxy - 5 - methyl - 2 - ethyl - 2,3 - dihydrofuran - 3 - one, 9.0 g of cysteine and 60 ml of water were heated in a round bottomed flask fitted with reflux condenser for 2 hours at 100°C. The reflux condenser was then removed and the contents cooled to room temperature. The resulting solution had a good roasted meat flavour.

EXAMPLE C4

A composition with a meat-like flavour was prepared by adding 100 ml of water to a mixture of 4.0 g of 4 - hydroxy - 2,5 - diethyl - 2,3 - dihydrofuran - 3 - one and 20.0 g of cysteine and heating the mixture at 93—100°C for 4 hours.

EXAMPLE C5

A mixture of 1.5 g of 4 - hydroxy - 5-methyl - 2,3 - dihydrofuran - 3 - one and 1.5 g of cysteine in 30 ml of water was heated at about 100°C for 2 1/2 hours. To the resulting solution was added 33 g of maltodextrin. The solution thus obtained was carefully freeze-dried. The powder obtained was used as a good beef flavour in soup or gravy.

EXAMPLE C6

5.0 g of 4 hydroxy - 2,5 - dimethyl - 2,3-dihydrofuran - 3 - one, 0.5 g of hydrogen sulphide and 100 my of water were placed in an autoclave and heated for 2 hours at 100°C. To the resulting solution was added 100 g of malto-dextrin. The solution thus obtained was carefully freeze-dried. The powder obtained was used as a beef flavour in soup.

EXAMPLE C7

1.6 g of 4 - hydroxy - 2,5 - dimethyl - 2,3-dihydrofuran - 3 - one, 8.0 g of glutathione and 50 ml of water were heated for 1 1/2 hours at 100°C in a round-bottomed flask fitted with a reflux condenser. To the resulting solution was added 5.0 g cysteine, and the mixture was again heated for 2 hours at 100°C. The resulting solution had a good roasted meat flavour.

EXAMPLE C8

A mixture of 4 g of powdered casein hydrolysate, 2 g of cysteine, 1 g of xylose, 1 g of 4 - hydroxy - 5 - methyl - 2,3 - dihydrofuran - 3 - one and 50 ml of water was heated in a flask with stirring for 2 1/2 hours

at 95°C. The solution thus obtained proved to have a good beef flavour.

EXAMPLE C9

A mixture of 5 g 4 - hydroxy - 5 - methyl-2,3 - dihydrothiophene - 3 - one/Cf. Example A1), 0.5 g of hydrogen sulphide and 50 ml of water was heated in an autoclave for 4 hours at 100°C and was subsequently allowed to cool. A product with a roasted meat flavour was obtained which was diluted to a volume of 1 litre, forming a liquid meat flavour.

EXAMPLE D1

A dry goulash soup was prepared by mixing the following ingredients:

	grams	
Dried meat	5	75
Salt	8	
Monosodium glutamate	2	
Protein hydrolysate	1	
Dried onion	5	80
Toasted onion	5	
Tomato powder	4	
Paprika powder	3	
Beef tallow	10	85
Corn starch	25	
Herbs and spices	4.	

According to this recipe two portions were prepared, each portion was used to make one litre of goulash soup by boiling it with 1 l of water for 20 minutes. To the first portion 0.5 ml of ethanol was added, whereas to the second portion 0.5 ml of ethanol containing 5 mg 3 - mercapto - 2 - methyl - tetrahydrofuran (Cf. Example A2) were added. Both soups were compared by a panel consisting of 12 persons. The majority of the panel preferred the soup in which the 3 - mercapto - 2-methyltetrahydrofuran had been incorporated. The panel indicated as the reason for this preference the more pronounced meat-like flavour of the relevant product.

EXAMPLE D2

A chicken soup was prepared with the following ingredients:

	grams	
Salt	7	105
Monosodium glutamate	1	
Meat extract	2	110
Protein hydrolysate	1	
Chicken bits	4	
Noodles	25	
Chicken fat	7	
Herbs and spices	4	

These ingredients were boiled with 1 l of water for 10 minutes, after which a solution of 0.1 mg of 3 - mercapto - 5 - methyltetrahydrofuran (Cf. Example A3) in 0.5 ml of ethanol was added. This resulted in a soup with a fuller, more pronounced chicken flavour, compared with the soup without added flavour.

EXAMPLE D3

A gravy was prepared from the following ingredients:

		grams
5	Potato starch	15
	Onion powder	2.5
	Monosodium glutamate	3
	Beef tallow	20
	Flour	15
10	Caramel	1.6
	Pepper	0.02
	Bay-leaves	0.02
	Clove	0.02
	Sodiumchloride	8
15	Protein hydrolysate	4
	Beef extract powder	2
	Tomato powder	1

The potato starch and flour were added to the molten beef tallow under continuous stirring. The other ingredients were well blended and likewise added to the beef tallow. The whole mixture was boiled in 1 l of water. The gravy so obtained was divided in two portions of 500 ml. To the first portion 0.5 ml of ethanol was added and to the second portion 2.5 mg of 3 - mercapto - 2 - methyl - 4.5 - dihydrofuran (Cf. Example A4) dissolved in 0.5 ml of ethanol.

Both gravies were compared by a panel consisting of 14 persons. The gravy containing 3 - mercapto - 2 - methyl - 4.5 - dihydrofuran was preferred by 12 persons because of its more pronounced meaty flavour.

EXAMPLE D4

A seasoning powder was prepared with the following ingredients:

		grams
	Meat extract powder	4
	Salt	5
40	Monosodium glutamate	3
	5 Ribo-nucleotides	0.1
	Protein hydrolysate	2
	Onion powder	0.2
	Celery salt	0.2
45	Pepper	0.02
	Malto-dextrin	0.3

A second seasoning powder was prepared according to this recipe. The only difference was that in this case the malto-dextrin contained 10 mg of 3 - thioacetoxo - 2 - methyl - 4.5 - dihydrofuran per gram (Cf. Example A4). 12 g of both seasoning powders were dissolved in 1 l of hot water and assessed by a panel consisting of 12 persons. The seasoning powder containing the 3 - thioacetoxo - 2 - methyl - 4.5 - dihydrofuran was unanimously preferred because of its more meaty flavour.

EXAMPLE D5

A gravy was prepared from the following ingredients:

		grams	
	Potato starch	15	
	Onion powder	2.5	
	Monosodium glutamate	3	65
	Beef tallow	20	
	Flour	15	
	Caramel	1.6	
	Pepper	0.02	
	Bay leaves	0.02	70
	Clove	0.02	
	Sodium chloride	8	
	Protein hydrolysate	4	
	Beef extract powder	2	
	Tomato powder	1	75
		72.16	

The potato starch and flour were added to the molten beef tallow at 60°C. under continuous stirring. The other ingredients were well blended and likewise added to the beef tallow. The whole mixture was boiled in 1 litre of water.

The gravy so obtained was divided into two portions of 500 ml. In the first portion 250 mg of malto-dextrin was dissolved; in the second portion 250 mg of the flavour powder prepared according to Example C5. Both gravies were assessed in a paired comparison test by a panel consisting of 12 persons.

The gravy containing the flavour powder was preferred by 10 out of the 12 tasters because of its more pronounced fried-meat flavour.

EXAMPLE D6

A basic composition for a dry beef soup was obtained by mixing the following ingredients:

		grams	
	Onion powder	0.5	
	Spice mix	0.5	100
	Fat	4	
	Dried soup vegetables	1	
	Monosodium glutamate	2	
	Modified potato starch	3	
	Noodles	20	105
	Salt	8	

One litre of water was added to the mixture and the whole was boiled for 5 minutes. The soup so obtained was divided in two portions of 500 ml. In the first portion 150 mg of malto-dextrin was dissolved and in the section portion 150 mg of the flavour powder prepared according to example C5.

Both soups were assessed in a paired comparison test by a panel consisting of 8 persons.

The soup containing the flavour powder had a characteristic beef flavour and was preferred by 7 out of the 8 testers.

EXAMPLE D7

- 5 Minced meat was prepared from the following ingredients:

	grams
Sausage meat	825
Salt	10
10 Whole egg	82.5
Bread-crumbs	82.5
	<hr/>
	1000

- The minced meat so obtained was divided into two portions of 500 g each. To the first portion was added a mixture of 10 g of bread-crumbs and 0.25 g malto-dextrin, and to the second portion a mixture of 10 g of bread-crumbs and 0.25 g of the flavour powder prepared according to Example C6. Meat balls prepared from each portion were fried in margarine for 30 minutes. The meat balls of both portions were assessed in a paired comparison test by a panel consisting of 8 persons. An unanimous preference was shown for the meat balls containing the flavour powder, because of the more pronounced fried meat flavour.

EXAMPLE D8

- 30 A basis for canned beef soup was prepared by adding the following ingredients to 4 litres of water:

	grams
Noodles	160
Herbs and spices	1.6
35 Tallow	80
Vegetables	400
Monosodium glutamate	16
Protein hydrolysate	16
Meat extract	16
40 Salt	64
Raw meat	400

- The total amount was divided into two portions, each of 2 litres. 1.4 g of the flavoured solution prepared according to Example C7 was added to one of the portions. The second portion which was used without further addition, served as a control. The mixtures thus obtained were canned in half litre tins and sterilised in an autoclave. A soup ready for consumption was prepared by adding an equal volume of water to the contents of each tin. After heating, both soups were served to a panel consisting of 19 persons for organoleptic testing. The soup with the flavour solution was preferred by 15 persons, because of its more pronounced meaty flavour.

EXAMPLE D9

- 60 One litre of gravy was prepared according to the method described in Example D5. This gravy was divided into two portions of 500

ml each. To one of the portions was added 0.2 g of the flavoured solution obtained in Example C 11, while the other portion was used without further addition. Both gravies were judged by a panel consisting of 9 persons. Of these panel 8 persons preferred the gravy with the flavour solution. A more pronounced meaty taste and a fuller flavour were given as reasons for the preference.

EXAMPLE D10

One litre of gravy was prepared according to the method described in Example D5. This gravy was divided into two portions of 500 ml each. To the first portion was added 0.5 g of the flavoured solution prepared according to Example C9, and to the second portion, 0.5 g of a solution prepared according to the method described in Example C9, except that the 1 g of 4 - hydroxy - 2,3 - dihydrofuran - 3 - one had been omitted. Both gravies were assessed in a paired comparison test by a panel consisting of 9 persons. The gravy portion containing the flavoured solution prepared, using all the ingredients of Example C8, was significantly preferred because of its more pronounced meat flavour.

EXAMPLE D11

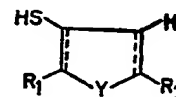
One litre of gravy was prepared according to the method described in Example D5. The gravy was divided into two portions of 500 ml each. To the first portion was added 250 mg of the flavour powder prepared according to the method described in Example C5, and to the second portion was added 12.5 mg of 4 - hydroxy - 5 - methyl - 2,3 - dihydrofuran - 3 - one. Both gravies were assessed in a paired comparison test by a panel consisting of 16 expert tasters. The gravy containing the flavour powder was preferred by 12 out of 16 persons because of its more pronounced fried-meat flavour.

EXAMPLE D12

A mixture of 1.0 g of 4 - acetoxy - 5 - methyl - 2,3 - dihydrofuran - 3 - one, 2.0 g of thioacetamide and 20 ml of water were heated together in a round bottom flask at 100°C for 4 hours. The reaction mixture was then allowed to cool. It had a good roast-beef flavour and was considered a favourable additive to a beef soup prepared according to Example D6.

WHAT WE CLAIM IS:—

1. A compound of the general formula



in which Y represents an oxygen or sulphur 115

- atom and R¹ and R² a hydrogen atom, a methyl group or an ethyl group, the total number of carbon atoms of R¹ and R² together being at least one, and in which no more than
- 5 one of the dotted lines between carbon atoms 2 and 3, or 4 and 5 represents either an additional carbon to carbon bond between these atoms, or that instead these carbon atoms carry each a hydrogen atom.
- 10 2. A compound according to claim 1, in which the dotted line between carbon atoms 2 and 3 represents an additional bond between said carbon atoms.
- 15 3. A compound according to claim 1, in which the dotted line between carbon atoms 4 and 5 represents an additional bond between said carbon atoms.
4. A compound according to claim 1, in which there are no additional bonds between
- 20 carbon atoms 2 and 3 or 4 and 5.
5. A compound according to claim 2, in which Y represents an oxygen atom.
6. A compound according to claim 2, in which Y represents a sulphur atom.
- 25 7. A compound according to claim 4, in which Y represents an oxygen atom.
8. A compound according to claim 4, in which Y represents a sulphur atom.
- 30 9. A compound according to claim 5, in which the total number of carbon atoms of groups R¹ and R² taken together is one.
10. 3 - Mercapto - 2 - methyl - 4,5 - dihydrofuran.
- 35 11. 3 - Mercapto - 5 - methyl - 4,5 - dihydrofuran.
12. A compound according to claim 6, in which the total number of carbon atoms of groups R¹ and R² taken together is one.
13. 3 - Mercapto - 2 - methyl - 4,5 - dihydrothiophene.
- 40 14. 3 - Mercapto - 5 - methyl - 4,5 - dihydrothiophene.
15. 3 - Mercapto - 2,5 - dimethyl - 4,5-dihydrofuran.
- 45 16. 3 - Mercapto - 2,5 - dimethyl - 4,5-dihydrofuran.
17. A compound according to claim 1, in which Y represents an oxygen atom.
18. A compound according to claim 1, in which Y represents a sulphur atom. 50
19. A compound according to claim 17, in which the total number of carbon atoms of groups R¹ and R² taken together is one.
20. Cis/trans 3 - mercapto - 2 - methyl-tetrahydrofuran. 55
21. Cis/trans 3 - mercapto - 5 - methyl-tetrahydrofuran.
22. 3 - Mercapto - 2,5 - dimethyl - tetrahydrofuran.
23. A compound according to claim 18, in which the total number of carbon atoms of groups R¹ and R² taken together is one. 60
24. Cis/trans 3 - mercapto - 5 - methyl-tetrahydrothiophene.
25. 3 - Mercapto - 2 - methyl - tetrahydrothiophene. 65
26. 3 - Mercapto - 2,5 - dimethyl - tetrahydrothiophene.
27. A foodstuff containing a flavouring amount of a compound as claimed in any of the preceding claims. 70
28. A foodstuff containing 1—8000 ppm of a flavouring compound as claimed in any of claims 1—26.
29. A foodstuff containing an effective amount of a precursor yielding a flavouring compound claimed in any of claims 1—26 upon preparation of the foodstuff in a form suitable for consumption. 75
30. A foodstuff according to claim 29, in which the precursor is an acetoxy substitution derivative of any of the substances claimed in claims 1—26. 80
31. A foodstuff according to claim 30, in which the precursor is 3 - thioacetoxy - 2-methyl - 4,5 - dihydrofuran. 85
32. A foodstuff according to claim 30, in which the precursor is 4 - acetoxy - 5 - methyl-2,3 - dihydrofuran - 3 - one.

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Chartered Patent Agent.

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